

## Cationic Rhodium(I) Complex-Catalyzed [3 + 2] and [2 + 1] Cycloadditions of Propargyl Esters with Electron-Deficient Alkynes and Alkenes

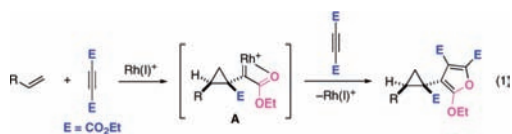
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Catalytic cycloadditions via metal carbene intermediates have been extensively studied, and a number of efficient methods are available.<sup>1</sup> However, the majority of reports involve cycloadditions with electron-rich unsaturated compounds because of the electrophilic nature of metal carbene intermediates.<sup>1</sup> Recently, several notable examples employing electron-deficient unsaturated compounds were reported.<sup>2–5</sup> For cyclopropanations of electron-deficient alkenes with diazo compounds, Ru(II)/salen<sup>2</sup> or Co(II)/porphyrin<sup>3</sup> complex-catalyzed reactions were reported. For cycloadditions of electron-deficient alkenes,<sup>4</sup> alkynes,<sup>5a,b</sup> and allenes<sup>5c</sup> with Fischer carbene complexes, Ni(0)-catalyzed cyclopropanations<sup>4</sup> and Rh(I)-catalyzed [3 + 2] cycloadditions<sup>5</sup> were reported. As an alternative method for the generation of metal carbene intermediates that is convenient as well as atom-economical, the 1,2-acyloxy rearrangement of terminal propargyl esters leading to alkenylcarbene intermediates catalyzed by Pd(II),<sup>6</sup> Ru(II),<sup>7</sup> and Au(I)<sup>8</sup> complexes was developed, while cycloaddition partners are limited to electron-rich unsaturated compounds.<sup>9</sup> Here we describe cationic rhodium(I) complex-catalyzed [3 + 2]<sup>10</sup> and [2 + 1] cycloadditions of propargyl esters with *electron-deficient alkynes and alkenes*.

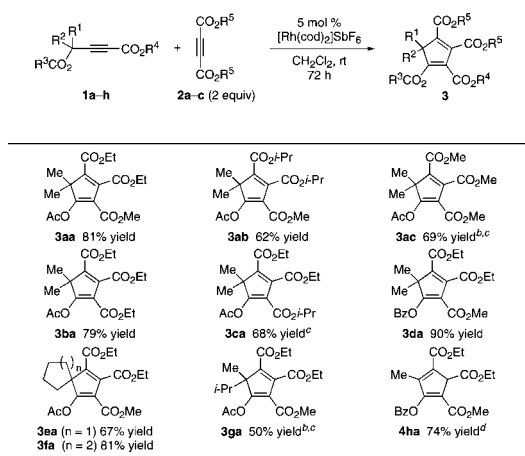
Our research group recently reported the cationic Rh(I)/(R)-Segphos [5,5'-bis(diphenylphosphino)-4,4'-di-1,3-benzodioxole]-catalyzed enantio- and diastereoselective cotrimerization of electron-rich alkenes and diethyl acetylenedicarboxylate, leading to furylcyclopropanes presumably through carbonyl-stabilized cationic Rh(I) carbene intermediate **A** (eq 1).<sup>11</sup>



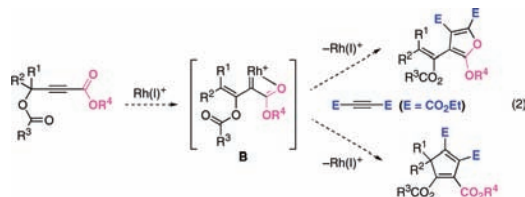
This result indicates the nucleophilic nature of Rh(I) carbene **A**.

On the other hand, it is well-known that the electrophilic cationic Rh(I) complex is able to activate alkynes through the formation of a complex with the  $\pi$  electrons of the alkyne triple bond.<sup>12</sup> Thus, we anticipated that the cationic Rh(I) complex would react with an alkoxy carbonyl-substituted propargyl ester to generate the carbonyl-stabilized cationic Rh(I) carbene intermediate **B** via the 1,2-acyloxy rearrangement; **B** would then react with diethyl acetylenedicarboxylate to yield the corresponding furan or cyclopentadiene through the [3 + 2] cycloaddition of the carbonyl or alkene moiety of **B** (eq 2):

**Table 1.** Rhodium-Catalyzed [3 + 2] Cycloaddition<sup>a</sup>



<sup>a</sup> [Rh(cod)<sub>2</sub>]SbF<sub>6</sub> (0.025 mmol), **1a–h** (0.50 mmol), **2a–c** (1.00 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) were used. Cited yields are of isolated products. <sup>b</sup> Catalyst: 10 mol %. <sup>c</sup> At 40 °C. <sup>d</sup> Determined by <sup>1</sup>H NMR spectroscopy because of the instability of the product toward silica gel chromatography.

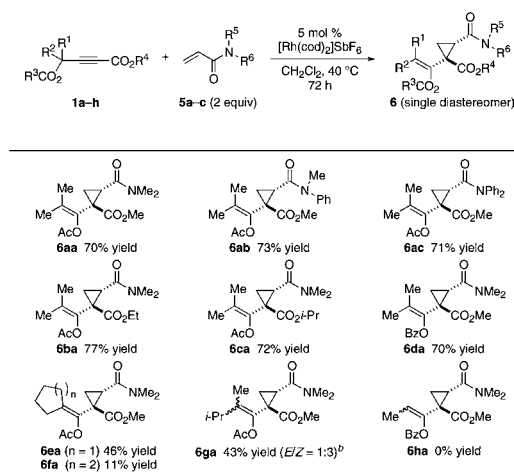


It was also expected that the alkoxy carbonyl group would facilitate the regioselective 1,2-migration of the acyloxy group because of the electronic polarization of the alkyne triple bond.<sup>13</sup>

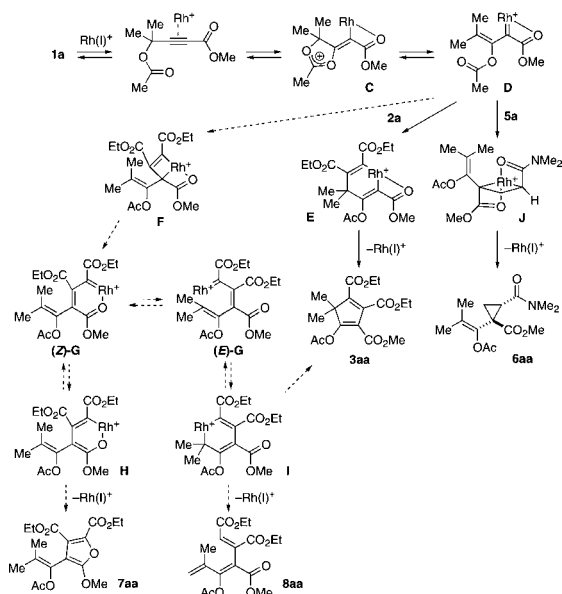
We first examined the reaction of methoxycarbonyl-substituted propargyl ester **1a** and diethyl acetylenedicarboxylate (**2a**) at room temperature using cationic Rh(I)/bisphosphine complexes, which are effective for the reaction shown in eq 1, but no cycloaddition product was generated. After screening catalysts and reaction conditions,<sup>14</sup> we were pleased to find that [Rh(cod)<sub>2</sub>]SbF<sub>6</sub> effectively catalyzed the [3 + 2] cycloaddition when excess **2a** and high concentration were employed, affording cyclopentadiene **3aa** in 81% yield (Table 1). Not only diethyl but also diisopropyl and dimethyl acetylenedicarboxylates reacted with **1a**, giving cyclopentadienes **3ab** and **3ac**, respectively, in good yields. With respect to propargyl esters, a variety of tertiary propargyl esters reacted with **2a** to yield cyclopentadienes **3ba–ga** in good yields.<sup>15</sup> Furthermore, a secondary propargyl ester was able to react with **2a** to yield the isomerized cyclopentadiene **4ha**. Not only electron-deficient alkynes **2** but also electron-deficient alkenes, acrylamides **5**,<sup>16</sup> were suitable cycloaddition partners (Table 2). *N,N*-dimethyl-,

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**Table 2.** Rhodium-Catalyzed [2 + 1] Cycloaddition<sup>a</sup>

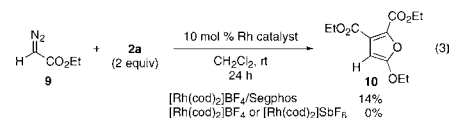
<sup>a</sup> [Rh(cod)<sub>2</sub>]SbF<sub>6</sub> (0.025 mmol), **1a–h** (0.50 mmol), **5a–c** (1.00 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) were used. Cited yields are of isolated products. <sup>b</sup> Catalyst: 10 mol %.

**Scheme 1**

*N*-methyl-*N*-phenyl-, and *N,N*-diphenylacrylamides reacted with **1a** at 40 °C to give cyclopropanes **6aa–ac** in good yields with perfect diastereoselectivity. The cyclopropanation of acrylamide **5a** with a variety of tertiary propargyl esters proceeded to afford cyclopropanes **6ba–ea** and **6ga** in good yields as single diastereomers, while *exo*-alkylidene-cyclohexane **6fa** was generated in low yield and a secondary propargyl ester failed to react with **5a**.

A plausible mechanism for the formation of **3aa** and **6aa** is shown in Scheme 1. A metallacyclopropane<sup>5,17</sup> of alkenylcarbene **D** with **2a** furnishes rhodacyclobutane **E**, and subsequent reductive elimination yields **3aa**. According to the proposed mechanism of the [3 + 2] cycloaddition of diazoacetates with alkynes to give furans,<sup>18</sup> the formation of furan **7aa** through intermediates **F**, (*Z*)-**G**, and **H** would also be possible. The metallacyclopropane reaction rather than the [2 + 2] cycloaddition of Rh(I)<sup>+</sup>/cod alkenylcarbene **D** with **2a** proceeds preferentially under the present reaction conditions, which might account for the observed chemoselective formation of **3aa** rather than **7aa**. Indeed, the Rh(I)<sup>+</sup>/cod complexes failed to catalyze the cycloaddition of

ethyl diazoacetate (**9**) with **2a**, while the Rh(I)<sup>+</sup>/bisphosphine complex did catalyze the cycloaddition (eq 3):



The formation of **3aa** through intermediates **F**, (*E*)-**G**, and **I** might also be excluded as a result of the stable Rh–O chelation in (*Z*)-**G** and the absence of possible β-hydride elimination product **8aa**. On the other hand, the [2 + 2] cycloaddition of intermediate **D** with **5a** furnishes rhodacyclobutane **J**. Subsequent reductive elimination yields **6aa**. Trans chelation of the ester and amide carbonyl groups to the cationic rhodium in intermediate **J** might account for the observed perfect diastereoselectivity.<sup>19,20</sup> Chelation of the alkenyl-acetate carbonyl group might be excluded because of the equilibration between intermediates **C** and **D**.<sup>13a,b</sup>

Future work will focus on further investigations into mechanistic insights and applications in organic synthesis.

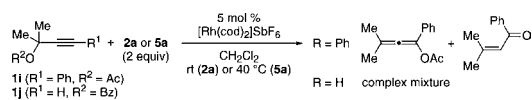
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**Supporting Information Available:** Experimental procedures, compound characterization data, optimization of reaction conditions, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) Ru(II), Pd(II), Pt(II), and Au(I) complexes failed to catalyze the reaction.

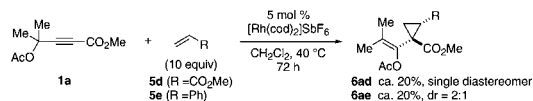
- (15) When phenyl-substituted propargyl ester **1i** was employed, the corresponding cycloaddition products were not obtained at all. The corresponding allene, generated through the 1,3-acyloxy rearrangement, and its hydrolyzed ketone were obtained as major products. The reactions of terminal propargyl ester **1j** led to a complex mixture of products:



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- (19) Indeed, the reaction of **1a** with methyl acrylate (**5d**) furnished cyclopropane **6ad** as a single diastereomer, but that with styrene (**5e**) bearing no carbonyl group furnished cyclopropane **6ae** as a mixture of diastereomers, although these products could not be isolated in a pure form:



- (20) The same diastereoselectivity was observed in the Ru(II)- (ref 2) and Co(II)-catalyzed (ref 3a) cyclopropanations of acrylates with **9**.

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